Dermal exposure to platinum group metals at a precious metal refinery: A pilot study.

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Author's contributions

This study was planned and executed by a team of researchers. Table 1 depicts the contributions of each of the researchers.

NAME	CONTRIBUTION
Ms. M. Barnard	• Sampling at the precious metal refinery. • Literature research, statistical analysis and writing of the mini dissertation.
Ms. A. Franken (Supervisor)	• Assisted in the designing, planning and reporting of the study. • Approval of the protocol. • Professional input and recommendations. • Reviewing of the mini-dissertation and documentation of the study.
Prof. J.L. du Plessis (Co-supervisor)	• Assisted with the planning of the study. • Assisted with the planning and approval of the protocol. • Professional input and recommendations. • Reviewing of the mini-dissertation and documentation of the study.

The following is a statement from the authors that confirms each individual's role in the study:

I declare that I have approved the article and that my role in the study as indicated above is representative of my actual contribution and that I hereby give my consent that it may be published as part of Marilize Barnard's M.Sc. (Occupational Hygiene) mini-dissertation.

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Ms. A. Franken (Supervisor) Prof. J.L. du Plessis (Co-Supervisor)

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List of abbreviations

ABEK cartridges	A - Organic vapours and gases with boiling points >65°C
	B - Inorganic gases excluding carbon monoxide
	E - Sulphur dioxide and acidic gases
	K - Ammonia and organic ammonia derivatives
ACD	Allergic Contact Dermatitis
BDL	Below Detection Limit
˚C	Degrees Celsius
cm^2	Square centimetre
e.g.	For example
etc.	Etcetera
FICO	Final Concentrate
HERAG	Health Risk Assessment Guidance
HSD-test	Honest Significant Difference test
IARC	International Agency for Research on Cancer
ICD	Irritant Contact Dermatitis
ICP-MS	Inductively coupled plasma mass spectrometry
IgE	Immunoglobulin E
IPA	International Platinum Association
Ir	Iridium
ISO	International Organisation for Standardization
MC-plant	Magnetic Concentrate plant

MDHS	Methods for the Determination of Hazardous Substances
ml	Millilitre
n	Sample size
OEL	Occupational Exposure Limit
OSHA	Occupational Safety and Health Administration
Os	Osmium
P3	Protection factor 3
%	Percentage
Pd	Palladium
PGMe	Platinum Groep Metale
PGMs	Platinum Group Metals
PPE	Personal Protective Equipment
PSS	Platinum salt sensitivity
Pt	Platinum
ng/cm^2	nano grams per square centimetre
$[(NH_4)^2PtCl_4]$	Ammonium tetrachloroplatinite
$[(NH_4)^2PtCl_6]$	Ammonium hexachloroplatinate
NORA	National Occupational Research Agenda
Rh	Rhodium
RSS	Rhodium Salt Sensitivity
Ru	Ruthenium
SC	Stratum Corneum
SI units	System International (units in the International System)

µm	Micrometre
WAO	World Allergy Organisation
WHO	World Health Organization

Preface

This mini dissertation is written in article format specifically for potential publication in the journal *Annals of Occupational Hygiene* and, therefore, conforms to the requirements preferred by the journal. For uniformity the same reference style is used throughout the entire mini-dissertation.

At the end of each chapter, references should be listed in alphabetical order and in-text references should be listed chronologically, using the Vancouver Style of abbreviation and punctuation:

For example:

- Agache P, Black D. (2004) Stratum corneum dynamic hydration tests. In Agache P, Humbert P, editors. Measuring the skin. Berlin: Springer-Verlag. p. 153-163. ISBN 3 540 01771 2.
- Baker DB, Gann PH, Brooks SM, *et al.* (1990) Cross-sectional study of platinum salts sensitisation among precious metals refinery workers. Am J Ind Med; 18: 653-664.
- Chamber of Mines of South Africa. (2010) Education: Platinum 2009. Available from: URL: http://www.bullion.org.za/content/?pid=86&pagename=Platinum (accessed 2 Aug 2011)

ABSTRACT

Background: Workers in a platinum group metals (PGMs) refinery are potentially exposed to various precious metals (iridium, osmium, palladium, platinum, rhodium and ruthenium) and their metal-salt compounds which may cause rhinitis, asthma, contact urticaria and conjunctivitis. Some cases revealed that sensitisation occurred in employees where it was not possible to detect any airborne soluble platinum or where the respiratory soluble platinum exposure was below the occupational exposure limit. It is unclear whether respiratory exposure or a combination of respiratory and dermal exposure may be involved in sensitisation and the possible elicitation of skin symptoms.

Objectives: To determine if dermal exposure to PGMs took place during the refining process and in the administration area by using a removal method and to compare dermal exposure on the different anatomical areas and in two different working areas, Areas A and B for each of the PGMs.

Methods: Dermal exposure samples were collected with a removal method using Ghostwipes^{TM}. The samples were collected from the palm of the hands, the wrists and the necks of the workers, before the shift started, before tea time, before lunch time and after the shift ended. The skin wipes were analysed for the PGMs (iridium, osmium, palladium, platinum, ruthenium and rhodium) according to Methods for the Determination of Hazardous Substances (MDHS) method 46/2, using Inductively Coupled Plasma-Mass Spectrometry.

Results: No published data is available on occupational dermal exposure to PGMs in a precious metals refinery. This study proved that dermal exposure to PGMs in the refinery took place and was quantified. The PGM dermal exposure results in general, were very low (measured in nano grams), with platinum having the overall highest exposure. Exposure also occurred the most frequently during the last two intervals of the day, before lunch time and at the end of the shift. Exposure on all three the anatomical areas that were tested in the study, varied much with the palm of the hands having the highest exposure levels. There were also variations in exposure between areas A and B due to the fact that the processes in these two areas differ.

Conclusions: It was confirmed that dermal exposure to PGMs took place at the precious metals refinery. The highest exposure took place before lunch time and towards the end of the shift. The metal to which the workers were exposed the most was platinum and the production area where the workers had the highest exposure to most of the metals was Area B.

Keywords: iridium, osmium, palladium, platinum, rhodium, ruthenium, skin exposure, sensitisation, wipe sampling, dermal.

OPSOMMING

Agtergrond: Werkers in 'n platinum groep metaal (PGMe) raffinadery word moontlik blootgestel aan 'n verskeidenheid platinum groep metale (iridium, osmium, palladium, platinum, rodium en rutenium) en hulle metaalsout verbindings, wat rinitis, asma, kontak urtikarie en konjunktivitis kan veroorsaak. Sommige gevalle het aangetoon dat sensitisering voorkom in werkers waar daar geen luggedraagde oplosbare platinum waargeneem kon word nie, of waar die luggedraagde oplosbare platinum blootstelling laer was as die beroepsblootstellings drempel. Dit is onduidelik of respiratoriese blootstelling of 'n kombinasie van respiratoriese en dermale blootstelling betrokke is by die sensitisering en die moontlike ontlokking van vel simptome.

Doelwitte: Om vas te stel of dermale blootstelling aan PGMe plaasvind gedurende die raffineringsproses deur gebruik te maak van 'n verwyderingsmetode en om dermale blootstelling op die verskillende anatomiese areas in twee verskillende werksareas, areas A en B te vergelyk vir elkeen van die PGMe.

Metodes: Dermale blootstellingsmonsters is versamel deur van 'n verwyderingsmetode gebruik te maak, met behulp van "Ghostwipes™". Die monsters is geneem op die palm van die hand, die gewrig en die nek van die werkers, voor die skof begin het, voor teetyd, voor middagete en voor die skof geëindig het. Die velveeg lappies is geanaliseer vir die verskillende PGMe (iridium, osmium, palladium, platinum, rodium en rutenium) volgens die metodes vir die bepaling van gevaarlike stowwe (MDHS) metode 46/2 met behulp van induktiefgekoppelde plasma-massa spektrometrie.

Resultate: Daar is geen vorige gepubliseerde data beskikbaar oor dermale blootstelling aan platinum groep metale in 'n edel metale raffinadery nie. Hierdie studie het bewys dat dermale blootstelling aan PGMe in die raffinadery plaasgevind het en gekwantifiseer was. Die dermale resultate was redelik laag oor die algemeen (gemeet in nano gramme), met platinum wat oor die algemeen die hoogste blootstelling het. Gedurende die laaste twee intervalle van die skof, voor etenstyd en aan die einde van die skof, het die meeste blootstelling plaasgevind. Daar was groot variasies in blootstelling op al drie die anatomiese areas wat in die studie getoets was met die palm van die hand wat die hoogste blootstelling toon. Daar was ook variasies in die blootstelling tussen produksie Areas A en B. Hierdie variasies kan heel moontlik toegeskryf word aan die verskillende prosesse wat in die areas plaasvind.

Gevolgtrekking: In hierdie studie is daar bevestig dat dermale blootstelling aan PGMe wel plaasvind in 'n edel metaal raffinadery. Die hoogste blootstelling het plaasgevind voor middagete en nader aan die einde van die skof. Die metaal waaraan die werkers die meeste blootgestel was, was platinum en die produksie area waar die werkers die hoogste blootstelling gehad het aan die meeste van die metale, was Area B.

Sleutelwoorde: iridium, osmium, palladium, platinum, rodium, rutenium, vel blootstelling, sensitisering, vel veeg metode, dermaal.

CHAPTER 1: INTRODUCTION

GENERAL INTRODUCTION

1.1. Introduction

The demand for platinum group metals (PGMs) in the world essentially rises out of the servicing of platinum requirements and the establishment of new capacity in the industry (PGMs) to make up losses suffered in the mining sector over the last few months in South Africa (Chamber of Mines of South Africa, 2014).

Workers in a PGM refinery are potentially exposed to various precious metals (iridium, osmium, palladium, platinum, rhodium and ruthenium) and their metal-salt compounds. Throughout the refining process, PGMs are sent through an oxidative leaching process to allow the metals to pass into the solution where after the recovery of the metals takes place by liquefying some of or all of the PGMs (Tatarnikov *et al*., 2004). Platinum is precipitated from the solution through the addition of ammonium chloride or hydrochloric acid and chlorine gas which then precipitates sensitising agents such as ammonium hexachloroplatinate from the solution (Phetla *et al*., 2010). The metals of the above mentioned salts are separated using precipitation and dissolution techniques. Both ammonium tetrachloroplatinate and ammonium hexachloroplatinate, present as compounds during the refining process, were found to be the main occupational sensitising agents among platinum refinery workers (Murdoch *et al*., 1986). This exposure can cause rhinitis, asthma, contact urticaria and conjunctivitis (Merget *et al*., 2000). Several case reports have been published concerning workers who were exposed to platinum compounds and experienced some of the symptoms of a type I hypersensitivity reaction (Murdoch *et al*., 1986; WHO, 1991; Calverley *et al.,* 1999; Merget *et al*., 2002).

In numerous studies, symptoms following occupational exposure to complex platinum salts have been revealed. Some of these symptoms are watery eyes, coughing, sneezing, wheezing, dyspnoea, itching and cyanosis which are characteristic of severe asthma and contact dermatitis (Cleare *et al.,* 1976; Cromwell *et al*., 1979; Baker *et al.,* 1990). When sensitised, these symptoms are collectively referred to as PSS (platinum salt sensitivity) or RSS (rhodium salt sensitivity) (Calverley *et al.,* 1995).

Traditionally, the focus was on the respiratory route of exposure in workplaces, but during the past decade there was more focus on the dermal route of exposure and it became more prominent in research (Maynard *et al*., 1997; Ngo & Maibach, 2010). The number of skin related clinical diagnoses for platinum exposure, reported in previous studies e.g. contact dermatitis, contact urticaria and hypersensitivity reactions, is relevant when considering the dermal route as a possible route of exposure (Cleare *et al.,* 1976; Murdoch *et al*., 1986; Venables *et al*., 1989; Merget *et al*., 2002; Christaudo *et al*., 2005). In a previous study it was suggested that infrequent dermal exposure could possibly lead to high levels of soluble platinum salts on the skin and that sensitisation occurred in employees where it was not possible to detect any airborne soluble platinum or where the airborne soluble platinum values were below the occupational exposure limit (OEL) (Maynard *et al*., 1997). Platinum salts have been reported to induce hypersensitivity reactions in workers with respiratory symptoms as well as dermal symptoms such as contact urticaria and contact dermatitis. This could be the result of sensitisation occurring at concentrations lower than the OEL or the possibility of an alternate route of exposure (Maynard *et al*., 1997; Christaudo *et al*., 2005). Maynard *et al.* (1997) suggested that it could possibly be the dermal route of exposure due to significant skin contact occurring during his study. This suggestion by Maynard *et al.* (1997) led to the question regarding dermal exposure in refinery workers (Maynard *et al*., 1997). In general, more researchers are observing the dermal route as a possible route of exposure to metals (Du Plessis *et al*., 2010; Hughson *et al*., 2010). It is unclear whether respiratory exposure or a combination of respiratory and dermal exposure may be involved in sensitisation and the possible elicitation of skin symptoms. For this reason it is important to establish whether precious metal refinery workers are exposed to PGMs through the dermal route of exposure and at what levels or concentrations the exposure takes place. This will also contribute to the small, but growing body of literature available on dermal exposure to sensitising metals, which is currently limited to primarily beryllium, cobalt, chromium and nickel (Maynard *et al*., 1997; Fenske, 2000; Lidén *et al.,* 2006; HERAG, 2007; Du Plessis *et al*., 2010; Hughson *et al*., 2010).

This pilot study was limited to only two high risk production areas in the refinery. It will serve as a means to determine if exposure through the dermal route takes place, because the airborne soluble platinum levels were consistently below the OEL, according to the legally required airborne monitoring that took place in the past.

1.2. Aims and Objectives

The aim of this study is to assess the dermal exposure of precious metal refinery workers to PGMs.

Specific objectives

- To determine if dermal exposure to PGMs occurred during the refining process, by using a removal method.
- To compare, statistically, the dermal exposure of the different anatomical areas (palm of hand, wrist and neck) for each of the PGMs.
- To compare, statistically, the dermal exposure in the different working areas (administration area and production areas A and B) of the refinery for each of the PGMs.

1.3. Hypothesis

Previous research has focused on respiratory exposure as the main route of exposure to various metals in refinery settings. Limited information is available on dermal exposure to these metals. It is hypothesised that workers at a precious metal refinery are exposed to quantifiable levels of PGMs via the dermal route of exposure.

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CHAPTER 2: LITERATURE STUDY

2.1. Introduction

As stated in Chapter one, there is an immense shortage of information concerning dermal exposure to PGMs in precious metal refineries. In most cases, these precious metals pose a health risk to refinery workers (Venables *et al*., 1989). Therefore the probability exists that some of the symptoms (itching, shortness of breath, etc.) experienced by these workers is as a result of dermal exposure or dermal and respiratory exposure simultaneously (Maynard *et al.,* 1997). Maynard *et al.* (1997) suggested that sensitisation took place through an alternate route than the respiratory route since airborne soluble platinum levels were below the OEL. They suggested that the dermal route may be a possible route of exposure to PGMs that would in the end lead to sensitisation (Maynard *et al.,* 1997). Chapter 2 provides a description of the PGMs, their mining, uses, measurement methods, exposure to and also the health effects that are associated with the different routes of exposure.

2.2. Mining of PGMs

Exposure to PGMs can take place during each and every one of the steps in the various processes of mining PGMs, but at the refinery the PGMs are more concentrated and in a form where it has the ability to cause health effects. That is why the refinery, where the PGMs are concentrated and then extracted, is the main focus in this study.

2.2.1. Ore Extraction:

The first step in mining of the PGMs is to extract the platinum ore out of the ground and get it into the process of separation (at the refineries). The aim of the extraction process is to enrich the matte to approximately 65% content of PGMs (Gouldsmith & Wilson, 1963). There are two methods to extract PGMs from the ground. The one is the “narrow reef method” which comprises of hand-held pneumatic drills to bore holes in the ground and filling them up with explosives and taking the ore out of the stope when it is free after blasting. The second method is the “mechanical mining method” or the “hybrid mining method” in which specialised drilling equipment (conventional hand-held pneumatic drills or low-profile machines equipped with specialised drilling equipment) are used to remove the ore from the ground and to load machines to transport the ore to the various refineries (Dachary, 2013).

2.2.2. Concentrators and smelters:

When the ore is extracted from the ground it is crushed and milled into smaller rock particles to expose the mineral content which may contain PGMs. These particles are mixed with reagents and some water in a froth flotation process, where air is pumped through the liquid. PGM-containing particles attach to bubbles created in the process, and then float up to the surface of the mixture. This flotation mixture is then removed altogether as a soapy froth (Chamber of Mines of South Africa, 2010). The PGMs that are not able to float in the mixture go through another flotation process through which it is also milled and dried. The rest of the froth concentrate mixture is then dried and melted in a furnace at a smelter at temperatures that can range between 1180 $^{\circ}$C – 1380 $^{\circ}$C (Hundermark *et al*., 2011). This process is to separate the valuable metals from the unwanted minerals, that are discarded as slag. The remaining matte is sent to the converters to remove the iron and sulphur (Chamber of Mines of South Africa, 2010).

2.2.3. Base Metal Refineries:

After mining, extraction, concentration and smelting processes, the PGMs must be refined. The base metals are removed from the converter matte by a combination of processes involving leaching and magnetic separation (Chamber of Mines of South Africa, 2010). The Base Metal Refinery consists of two sections, the Base Metal Plant and the Magnetic Concentrated Plant (MC Plant) (Personal communication – onsite occupational hygienist, J. Olivier). Concentrated matte from the Converters arrives at the Base Metal Refinery from where it goes straight to the milling section. Milling of the base metal matte takes place to liberate the minerals for further treatment. The matte goes through a de-watering process where after the nickel and cobalt are separated from the PGMs by using a series of electrolytic techniques (leaching processes) (Chamber of Mines of South Africa, 2010). In these processes nickel and cobalt and their by-products are produced. The following stage is the leaching of copper out of the nickel leach residue from which copper metal is produced. The copper leach residue is upgraded by the leaching of copper, iron, sulphur and amphoterics, which produces a high grade PGM concentrate. Base metals are valuable to the company and form part of the PGM-extraction process (Chamber of Mines of South Africa, 2010).

2.2.4. Precious Metal Refineries:

This is the last stage in platinum refining, also one of the most complex of metal separations. The process from this stage onward is almost entirely chemical because of the rapid concentration of the PGMs (Gouldsmith & Wilson, 1963). Precious metal refining processes have changed significantly over the last few decades. Roasting of the PGM concentrate was part of some of the older processes. This process resulted in oxidising the ruthenium, rhodium and iridium and making them insoluble in aqua regia. Then, by using a series of precipitations the palladium, platinum and gold were dissolved and separated. The residual residue was upgraded by leaching and pyro-metallurgical processes and thereafter it was separated into individual metals. The final stage of the process was purification of all the metals through repeated precipitation and dissolution (Chamber of Mines South Africa, 2010).

Today the separation chemistry of PGMs is among the most challenging of metal separations. The first step is when the matte, received from the Base Metals Refinery, is roasted and sent through a high pressure leaching and ion exchange process (combined with solvent extraction and distillation) to remove the last traces of copper, nickel, iron and sulphur (Gouldsmith & Wilson, 1963; Chamber of Mines of South Africa, 2010). This is where the enriched matte containing only PGMs is brought into solution for further separation and in the end refining (Gouldsmith & Wilson, 1963; Chamber of Mines of South Africa, 2010). The next stage is solvent extraction of each of the PGMs from the solution. This process can briefly be explained as the precipitation of the metals as salts which is followed by recrystallisation and calcinations under controlled conditions to produce the PGMs in the form of powders. The soluble metals (gold, palladium and platinum) are dissolved in ammonium chloride (which then precipitates ammonium hexachloroplatinate) or hydrochloric acid and chlorine gas and are obtained first in the process. The insoluble PGMs (rhodium, osmium, ruthenium and iridium) are obtained last in the process (Seymour & O'Farrell, 2001).

The precious metals refinery is a semi enclosed refinery; this means that some of the working areas are isolated from others, some are totally enclosed or confined, some are open and others are partially enclosed. The two working areas that were included in this study were Area A which was open and Area B which was enclosed. Some of the instances where dermal exposure is expected to take place in the refinery, is when dismantling of equipment during shut down periods is done, with the digging of glove boxes, dropping of hoppers, cleaning of filters and with the flushing and loading of tanks (Personal communication – onsite occupational hygienist, C. Venter).

From an observation it was concluded that workers in the production areas of the refinery wear two-piece 100% cotton overalls, cotton and rubber gloves, safety boots, glasses, hardhats and earplugs. The overalls protect the bodies of the workers from acid spills and other liquid risks. The overalls cover the arms and the gloves cover the hands, whilst the wrist of the workers is sometimes exposed due to the overall and glove coming together in this area. Other anatomical areas which are totally exposed are the necks and the faces of the workers. The airstream helmets worn in some production areas only cover a part of the neck and face and in the rest of the areas the necks and faces are totally exposed.

2.3. Properties of the PGMs

PGMs (iridium, osmium, palladium, platinum, rhodium and ruthenium) are transition metals and also metallic elements that are chemically very similar (Giandomenico, 1996).

2.3.1. Platinum (Pt):

Platinum is a third row transition metal and also part of the family of PGMs (Giandomenico, 1996). The appearance of platinum metal is silver-grey with a high commercial value because of its properties as an oxidation and reduction catalyst and its resistance to corrosive agents. Platinum is resistant to high temperature corrosion (O'Neil, 2001).

2.3.2. Palladium (Pd):

Palladium is a very rare naturally white precious metal with the lowest melting point of all the PGMs and is also the least dense (IPA, 2012). It is very strong and durable and also resistant to high temperatures. Palladium is usually recycled from scrapped catalytic converters (Jorgensen, 2009). With the limited supply of palladium because of its various applications, it generally results in a considerable investment interest for many investors (IPA, 2012).

2.3.3. Rhodium (Rh):

Rhodium is a silvery-white transition metal, almost like platinum, and also one of the world's most expensive precious metals. Rhodium can only be dissolved in sulphuric acid. Rhodium has great value and the cost of its separation is generally very expensive (Bush, 1991). Rhodium is hard to work with but very valuable alone and in alloys (Latini *et al.,* 2010). It is generally alloyed with palladium or platinum and applied in corrosive resistant and high temperature coatings (IPA, 2012).

2.3.4. Iridium (Ir):

Iridium is a silvery-white metal, similar to rhodium, and is hard and brittle with low ductility. Iridium is one of the densest elements and is also very corrosion resistant even at very high temperatures (2000 °C) (IPA, 2012). It is used as a hardening agent in platinum alloys (Greenwood & Earnshaw, 1997). Iridium, similar to rhodium, is very hard to work with but very valuable alone and in alloys (Latini *et al.,* 2010).

2.3.5. Ruthenium (Ru):

Ruthenium is a precious metal that is generally rare in the earth's crust (IPA, 2012). Ruthenium usually makes out a very small part of platinum ores and its annual production is only approximately 20 ton. With the addition of a small amount of ruthenium the corrosion resistance of titanium is increased remarkably (Hammond, 2005).

2.3.6. Osmium (Os):

Osmium is a blue-grey or blue-black transition metal found in nature as an alloy (IPA, 2012). It is also a hard, brittle metallic element that is generally used as a platinum hardener (IPA, 2012). Osmium is not affected by water or acids and dissolves in alkalis. It is very rare and expensive as a result. Its alloys with other PGMs are employed in applications where durability and hardness are needed (Hammond, 2005).

2.4. Uses of Platinum Group Metals

Worldwide production of PGMs has risen steadily over the years until recently, with the industry being hampered by labour unrest in South Africa (Wiseman & Fathi*,* 2009; Chamber of Mines of South Africa, 2014). PGMs play a vital role in South Africa and in the rest of the world concerning transportation, power generation and healthcare (IPA, 2012). It also has a variety of other uses in glass, industrial, electrical, chemical and pharmaceutical applications (Wiseman & Fathi, 2009).

2.4.1. Auto catalysts:

Catalytic converters are fitted into motor vehicle's exhaust systems to reduce their polluting effects. The converter mainly consists of a honeycomb which is covered with rhodium, platinum and sometimes palladium. As engine exhausts pass through the converter at temperatures of approximately 300 $^{\circ}$C, the PGMs converts nitrogen oxide along with carbon monoxide and unburnt hydrocarbons into carbon dioxide, nitrogen and water (Chamber of Mines of South Africa, 2010).

2.4.2. Jewellery:

Approximately 20% of the world's platinum production is invested in the jewellery market (IPA, 2012). PGMs are very popular in the jewellery industry, explicitly in Japan. PGMs are being favoured in the jewellery industry, over gold and silver (Chamber of Mines of South Africa, 2010).

2.4.3. Investment:

Platinum coins and medallions are being launched on to the market by various marketing agents such as Johnson Matthey. The Isle of Man Noble, Canadian Maple Leaf and the Australian Koala are some of the front runners in the legal coin investment sector (Chamber of Mines of South Africa, 2010).

2.4.4. Industry:

Platinum tipped spark plugs are making an entrance into the market, with improved combustion and fuel efficiency. Fifty percent of the annual palladium and ruthenium demands are associated with the electrical and electronics industry. In the chemicals industry, PGMs are currently used as intermediates in the process of producing nitric acid that is essential for explosives and fertilizer manufacturing. PGMs are also used in the manufacturing of products such as glass fibre and in the glass industry. Some of the PGMs are also vital ingredients in the petro-chemical industry where they play a role in the manufacturing of higher octane fuels (Chamber of Mines of South Africa, 2010).

2.4.5. Medicine:

Some of the PGMs have been used in the medical industry, for instance where platinum by-products are used in the treatment for cancer and where palladium is becoming a substitute for gold in dentistry (Chamber of Mines of South Africa, 2010).

2.4.6. Fuel cells:

Platinum catalysts are used in clean and efficient fuel cells, to convert chemical energy into electrical energy (Chamber of Mines of South Africa, 2010).

2.5. Skin anatomy and barrier function

Absorption of metals through the skin is governed by numerous interconnected mechanisms and also sometimes influenced by various exogenous and endogenous factors such as skin condition and temperature, barrier function, age, gender, race, anatomical area and sweating (Hostynek, 2003; Stefaniak *et al*., 2013). The skin is not a complete resistant barrier. There are three potential penetration pathways through which substances can enter the skin barrier: 1) intracellular, 2) intercellular, and 3) follicular routes. One of these routes or a combination of more than one of them can be the pathway or route through which exposure to PGMs takes place. Therefore, it is important to discern the skin's histology and function. The skin anatomy will be described as an introduction to skin barrier function and it will be followed with a description of the factors influencing barrier function.

2.5.1. Skin anatomy:

The skin is the largest organ in the body and it consists of various layers with specific functions. The stratum corneum is the outer layer of the skin and consists of multiple corneocyte cells that have no nucleus or organelles (Sandilands *et al*., 2009; Hogan *et al*., 2012). These corneocytes protect the skin against external chemicals and physical stressors as it is in constant contact with the environment. The skin is a complex membrane which consists of two separate layers, the epidermis and the dermis. The epidermis is the outer layer and also the biggest defence mechanism against external stressors. The dermis is situated underneath the epidermis and consists of fibrous connective tissue. Underneath the dermis is subcutaneous tissue called the hypodermis which anchors the skin to the underlying structures (Marieb *et al*., 2007).

The epidermis, which is self-renewing, is separated from the dermis via a basement membrane (McGrath *et al.*, 2004; Bouwstra *et al*., 2006; Rice *et al.,* 2008). The epidermis-dermis junction provides the mechanical support and acts as a barrier against exchange of cells and large molecules. Collagen is one of the primary elements of the dermis which provides the skin with great tensile strength. Fibroblast cells, mast cells and histiocytes are also present in the dermis along with richly supplied blood vessels (McGrath *et al.*, 2004).

Several types of cells are present in the epidermis layer of the skin; they are keratinocytes, melanocytes, Langerhans-, Merkel- and inflammatory cells (McGrath *et al.*, 2004). The keratinocytes are attached to the basement membrane in the epidermis by hemidesmosomes and they are attached to each other by desmosomes. During the final step of the keratinocytes' differentiation, they undergo profound changes in their structure and are transformed into corneocytes of the stratum corneum (McGrath *et al.*, 2004; Proksch *et al.*, 2008). The corneocytes are embedded in an intracellular matrix and are tightly connected to each other with adjacent cells (Agache, 2004; Proksch *et al.*, 2008). The stratum corneum consists of 6 to 47 layers of corneocytes and its thickness ranges from 8-20 µm (Agache, 2004).

2.5.2. Skin barrier function:

The barrier in the skin forms a double-sided protective layer, it prevents penetration of unwanted substances through the skin (to the inside) and also loss of body fluids (to the outside) (Agache, 2004; Proksch *et al.*, 2008). It originates in the stratum corneum and forms a "brick-and-mortar" array where the corneocytes represent the bricks and the intercellular lipids represent the mortar. The extracellular lipids have a unique composition; they are composed of long-chain ceramides, free fatty acids and cholesterol (Bouwstra *et al.,* 2006; Proksch *et al.*, 2008). These lipids are positioned parallel to the cell surface and form lipid lamellar bilayers (Proksch *et al.*, 2008). When the skin barrier is disturbed through e.g. a hazardous chemical substance, a repair response is immediately initiated to recover the damage or to restore the disturbance in the barrier function.

2.6. Occupational exposure

Chronic exposure involving respiratory, dermal and oral routes plays an important role in occupational settings. Following inhalation, the dermal route of chemical exposure is of the biggest concern (Ngo & Maibach, 2010).

The greater interest in the skin as one of the main routes of exposure for potentially toxic substances and as a target organ, has grown rapidly in the field of dermatotoxicology (Merk *et al*., 2006; Karan *et al.,* 2009). Platinum salts (soluble) can affect the body if they are ingested, inhaled or come into contact with the skin or eyes. The most prevalent route of exposure in occupational settings is inhalation; this is also the route that has been researched most frequently. Inhalation is the respiratory intake of airborne particles through the mucosal lining of the trachea or the alveoli of the lungs and it occurs when particles such as soluble and insoluble platinum are propelled into the air (naturally or by mechanical forces) and into the breathing zone. The dermal route is when substances are deposited onto skin or comes into contact with the skin or when a part of the body is submerged into a substance and in this way penetrates the skin surface (Schneider *et al*., 2000). Compared to the development of inhalation methods, there is still very little progress made towards standardisation in the dermal field of study (Schneider *et al.,* 1999). Schneider *et al*. (1999) emphasises the necessity to make use of a reliable terminology based multi-compartment model of the process leading us from the source of exposure to the surface of the skin where the exposure takes place. The model also emphasises the importance of measuring exposure in the different compartments and it describes uptake as a result of transport of mass of the contaminant between the different compartments (air, surface contaminant, outer and inner clothing contaminant and skin contaminant layer compartments) (Schneider *et al.,* 1999). Possible routes suggested by Schneider *et al*. (1999) through which dermal exposure can take place are:

- The contaminant can become airborne and then come into contact with the skin.
- The contaminant can become airborne and then come into contact with the clothes and from there get onto the skin.
- The contaminant can be on a work surface and from there get onto the skin.
- The contaminant can be on a work surface and from there get onto the clothes and from there, onto the skin.
- The worker can touch the source of exposure directly and get contaminant on the skin.
- The contaminant can also spread to different parts of the skin e.g. if the hands are contaminated and the worker touches his face, the face becomes contaminated.

The general outcome of occupational exposure to PGMs is adverse health effects in the respiratory tract and the skin with the potential of lowering the quality of life, contributing to a disabling illness. No cancer bio-assays for platinum or anti-tumour drugs are available but according to mutagenicity assays, there is a possibility that carcinogenic activity may arise; similar to that of cisplatin (Sanderson *et al.,* 1996). The main interest of this study, concerning occupational PGMs exposure is to determine if exposure takes place through the dermal route and if so, to what extent.

2.6.1. Dermal exposure:

There is very little information available on dermal exposure to metals such as PGMs (Maynard *et al*., 1997; Christaudo *et al*., 2005), and even less on dermal exposure to PGMs at a precious metal refinery. That is why it is necessary to obtain information on dermal exposure to PGMs in a precious metal refinery to protect workers' health. The interest in the skin as one of the main routes of exposure to potentially toxic compounds has grown rapidly in the field of dermatotoxicology (Liden *et al*., 2006; Ngo & Maibach, 2010). When the skin comes into contact with a chemical or with airborne materials, dermal exposure (absorption) takes place and a reaction may arise (Ngo & Maibach, 2010).

Previous research on PGMs reported levels of respiratory exposure and symptoms workers experienced as a consequence of the respiratory exposure. A number of these symptoms were consistent with dermal exposure, e.g. contact dermatitis, contact urticaria and itching (Cleare *et al.,* 1976; Murdoch *et al*., 1986; Venables *et al*., 1989; Merget *et al*., 2002; Christaudo *et al*., 2005). In some cases where workers were monitored, they were sensitised although the concentration of airborne particles measured was below the occupational exposure limit (Maynard *et al.,* 1997). This may signify that sensitisation occurred at concentrations lower than the occupational exposure limit; due to very high short term exposure or that there was an alternate route of exposure via the skin due to skin contact (Maynard *et al*., 1997).

2.6.2. Respiratory exposure:

Inhalation of certain particles can have numerous pathological effects on the respiratory tract and it can affect organ systems such as the nervous and cardiovascular systems (Bonner, 2007). Several case reports have been published concerning workers who were exposed to platinum compounds by inhalation and now suffer from the symptoms consistent with platinum-specific allergenic sensitisation (WHO, 1991; Maynard *et al*., 1997). Halide platinum complexes are harmful when inhaled, especially when they contain a chloride compound (Cleare *et al*., 1976). Research done in a platinum refinery revealed that 23.1% of the workforce reported symptoms such as conjunctivitis, coughing, rhinitis and dyspnoea and that work related symptoms were more prominent in the workers with high exposure to platinum (Bolm-Audorff *et al*., 1992). In another platinum refinery, 44% of the workforce reported symptoms such as rhinitis, 29% asthma and chronic bronchitis (Brooks *et al.*, 1990). Hunter *et al*. (1945) also observed symptoms similar to these mentioned above in a precious metal refinery. All of these studies reveal symptoms consistent with dermal exposure although only respiratory exposure was measured. This suggests the dermal route together with the respiratory route can contribute to sensitisation occurring and that the dermal route could be a possible route of exposure to PGMs.

2.7. Health effects

There is no information available on PGM dermal exposure in precious metals refinery settings. A majority of the studies were done on respiratory exposure and the effects thereof.

2.7.1. Dermal health effects

2.7.1.1. Sensitisation and dermatitis

Contact dermatitis is one of the most regularly encountered occupational diseases amongst workers. Some of the symptoms experienced as a result of contact dermatitis are vesiculation on skin areas that made direct skin contact with a chemical, erythema, scaling and indurations (Ngo & Maibach, 2010). Dermal exposure was recognised, by the 1996 National Occupational Research Agenda, as a key component in dermatitis (allergic- and irritant dermatitis) (NORA, 1996; Fenske *et al*., 2000).

There are two subclasses of contact dermatitis namely irritant contact dermatitis (ICD) and allergic contact dermatitis (ACD). Both of these have similar clinical qualities (Ngo & Maibach, 2010). Allergic contact dermatitis (when in contact with some metals) is a frequently encountered problem that in some cases can cause morbidity to workers (Garner, 2004). Contact dermatitis represents a delayed-type hypersensitivity reaction (Type IV).

Sensitisation is a reaction of the body when exposure to a substance takes place, which elicits a response in the immune system. Sensitisation occurs when an allergen or chemical is absorbed through the skin or the respiratory tract and activates an immune response which can be recalled with a subsequent encounter with the allergen or chemical. These allergens are of a low molecular weight which gives them the ability to penetrate the stratum corneum and bind to keratinocytes (skin proteins) (Yunginger, 2003). This change in the keratinocyte surface makes recognition by the Langerhans cells in the epidermis, possible. At this stage the allergen or chemical binds to the Langerhans cells and is taken up in the lymph nodes where it is presented to CD4 T-cells. When re-exposure to the allergen or chemical occurs, the Langerhans cells will present the allergen or chemical to the T-cells again, within a period of 24 hours. After 48 hours, an inflammatory reaction to the allergen or chemical will take place (Mydlarski *et al*., 2003). The severity of the allergic reaction will depend on the exposed person's sensitivity to the allergen or chemical and also the concentration absorbed through the skin (Bigby *et al.,* 1991).

Platinum salts (tetrachloroplatinate and hexachloroplatinate) are potential sensitisers (Roberts, 1951; Parrot *et al.,* 1969; Cleare *et al*., 1976). Small doses of platinum salts bring forth reactions in sensitised workers (Cleare *et al*., 1976). Platinum salts cause an immediate reaction (Type I) when sensitisation occurs unlike some of the other PGMs that cause a delayed reaction (Type II). Metal allergy can develop as a result of prolonged skin contact with metal ions and this has the ability to lead to some form of dermatitis in workers (Thyssen & Ménne, 2010).

2.7.2. Respiratory health effects

While breathing, particles in the air are propelled into the respiratory tract, if the particles are harmful, they may have the potential to cause illnesses such as lung diseases (bronchitis, asthma, etc.), that can lead to a lifetime of suffering. Platinum salts and halide complexes, encountered by refinery workers, are known to induce hypersensitivity or toxicity reactions in combination with respiratory symptoms such as asthma and rhinitis (Cromwell *et al.,* 1978; Merget *et al*., 2002; Christaudo *et al.,* 2005). In some instances, when respiratory exposure to a substance takes place, the body has a Type I hypersensitivity reaction which elicits a response in the immune system, called sensitisation. Sensitisation occurs when an allergen enters the respiratory tract and is absorbed; this activates an immune response which can be recalled with every encounter thereafter with the same allergen (WAO, 2003).

2.7.3. Other health effects

2.7.3.1. Carcinogenicity

There is no information available on the carcinogenicity of platinum, halogenated platinum complexes (Nordberg *et al.,* 2007) and the other platinum group metals in humans or animals. None of the PGMs are listed as carcinogens in the International Agency for Research on Cancer monographs.

2.7.3.2. Liver, spleen, kidneys and bone

When soluble or insoluble platinum compounds have been absorbed into the body, these compounds tend to accumulate in organs such as the liver, spleen, kidneys and bone (Yoakum *et al*., 1975; Reichlmayr-Lais *et al*., 1992). In animal studies, PGMs has chronic effects that are characterised by the reduction in body mass and content of haemoglobin in the blood, by (i) disturbances of the protein-synthesising function of the liver, (ii) decreased cholinesterase activity in the blood, and (iii) impaired carbohydrate and lipid metabolism which reduces the concentrating capacity of the liver (Rochchin *et al*., 1984).

2.8. Dermal exposure monitoring

The procedure through which dermal exposure is assessed, the removal method, is an intricate task (HERAG, 2007). Dermal sampling of the anatomical areas on which measurements are taken are mainly narrowed down to the hands (palms and finger tips), forearms, neck and forehead (Brouwer *et al*., 2000).

2.8.1. Available methods

There are three strategies that were used in the last few decades for dermal sampling, namely interception methods, fluorescent tracer methods and chemical removal methods (Du Plessis *et al*., 2008).

2.8.1.1. Interception methods

This method consist of a collection medium (e.g. patches, gloves or whole body suites) that is placed on the clothing or skin, which in its own way retains contaminant in a similar manner as the skin, which is then subsequently analysed for the contaminant (Du Plessis *et al*., 2008).

a. Limitations

- With patch sampling the patches only represent a proportion of the body's surface area and because of this an over- or underestimation of exposure can easily be made. Estimation errors can also be made because the adherence of contaminants to human skin and to patches varies.
- When it comes to cotton glove sampling the possibility of tearing the glove exists, which would make the hand prone to direct exposure to contaminants and this would lead to a misrepresentation of the actual everyday exposure, and analysis of the whole glove would make it more expensive.
- As with analysis of the gloves, the analysis of a full body suit is also very expensive. The suits might also be susceptible to breakthrough, and the wearer may suffer from heat stress, depending on the environmental conditions (Du Plessis *et al*., 2008).

b. Advantages

- The interception method is fairly easy to use when compared to other skin methods.
- With whole body suit sampling no assumptions would be made concerning distribution of the contaminant on the suit (Du Plessis *et al*., 2008).

2.8.1.2. Fluorescent tracer methods

This method consists of a fluorescent tracer which is added to a specific production process where exposure patterns are analysed visually under fluorescent light (Du Plessis *et al*., 2008).

a. Limitations

- This is a very costly method to follow (Du Plessis *et al*., 2008).
- It is a method that monitors larger areas using sensitive video cameras in combination with image analysis software (Cherrie *et al.,* 2000). One would also have to add a tracer to a certain process which could be costly.

b. Advantages

- This method can be very useful in dermal exposure assessments because it can identify unrecognised exposure pathways and measures actual skin loading levels (Du Plessis *et al*., 2008).

2.8.1.3. The removal method

Involves removal of the contaminant on the upper skin layer by mechanical forces (wiping over the skin) and wet chemical action.

For this, skin wipes or washing solutions are used (Du Plessis *et al*., 2008). Wipe sampling is one of the most commonly used sampling methods that provide useful information about the mass of contaminant on a certain surface. The removal method, with Ghostwipes^{TM}, as the sampling media in this study, was reported on by the Occupational Safety and Health Administration's Method ID125G, to be very successful when removing metals from surfaces (OSHA, 2002). Skin wipe sampling has been used successfully to quantify exposures to a variety of metals including nickel, cobalt, beryllium and chromium. (Davis *et al*., 1983; Fenske, 1993; Schneider *et al*., 2000; Lidén *et al*., 2006; Day *et al*., 2007; HERAG, 2007; Du Plessis *et al*., 2010).

a. Limitations

- Skin wipe sampling is limited to hands, neck, forearms and forehead.
- This method only gives a rough estimate of the mean exposure loading, because only some areas are wiped and the wiping method could vary from one person taking the samples to the next (ISO, 2011).
- There is no standard procedure to follow for the number of wipes to take and the amount of force to use when taking them (Du Plessis *et al*., 2008).

b. Advantages

- Skin wipe sampling have been successfully used in various studies (Du Plessis *et al*., 2008; HERAG, 2007; Du Plessis *et al*., 2010; Christopher *et al*., 2011).
- This method is easy to use, whereas some of the other methods are more complex to use and do not give an idea of what the concentration was.

If and to what extent dermal exposure to PGMs occurs, is still a topic that needs to be researched, especially because some studies mention the dermal route as a possible route of exposure to metals that could contribute to sensitisation (Maynard *et al*., 1997; Fenske, 2000; Lidén *et al.,* 2006; HERAG, 2007; Gregory *et al*., 2009; Du Plessis *et al*., 2010; Hughson *et al*., 2010). There are various methods developed to measure metal exposure on a skin surface. Whereas, in this pilot study, a wipe sampling method was used to evaluate skin exposure to PGMs in refinery workers.

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- This article exceeds the limit of 5000 words (excluding the abstract and references) because it was completed for exam purposes and is therefore done very thoroughly.
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- The preferred practice is that persons should only be named as authors if they have made significant identifiable intellectual contributions to the work.
- Keywords should be given after the list of authors.
- Sampling surveys should be planned using modern statistical principles so that the quality of the data is good enough to justify the inferences and conclusions drawn.
- Units and symbols: SI units should be used, though their equivalent in other systems may be given as well.
- Tables: Tables should be numbered consecutively and given a suitable caption, and each table typed on a separate page. Footnotes to tables should be typed below the table and should be referred to by superscript lower case letters
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Emerg Infect Dis [serial online] 1995 Jan–Mar; 1(1). Available from:
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CHAPTER 3: ARTICLE

Dermal exposure to platinum group metals at a precious metal refinery: A pilot study

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3.1. Abstract

Background:

Workers in a platinum group metals (PGM) refinery are potentially exposed to various precious metals and their metal-salt compounds, through the respiratory and dermal routes. This exposure can result in conjunctivitis, asthma, rhinitis and contact urticaria. Previous studies indicated that sensitisation occurred in employees where it was not possible to detect any airborne soluble platinum exposure or where concentrations were below the occupational exposure limit (OEL). It is unclear whether respiratory exposure, dermal exposure or a combination of both may be involved in sensitisation to PGMs and the possible elicitation of skin symptoms.

Objectives: To assess dermal exposure to PGMs during the refining process using a removal method and to compare dermal exposure for each of the PGMs on the different anatomical areas of workers in two different processing areas in the refinery.

Methods: Dermal exposure samples were collected by using Ghostwipes^{TM}. The samples were collected from the palm of the hand, the wrist and the neck of workers, working in two production areas (Area A and B) and in the administration area. The samples were collected before the shift started, before tea time, before lunch time and at the end of the shift. The wipes were analysed for all of the PGMs using Inductively Coupled Plasma-Mass Spectrometry.

Results: In this study, the wipe removal method using Ghostwipes^{TM}, confirmed dermal exposure to five of the six PGMs of which platinum exposure was the highest based on the geometric means. Although the majority of the samples taken in this study was below the detection limit, the possibility of exposure taking place still exists, as the detection limits of the prescribed analytical methods are very high for some of the metals. The pre-shift exposure levels could be attributed to contamination in the change houses or skin loading from a previous shift. The high levels of exposure before lunchtime were due to the workers performing tasks where exposure to PGMs was possible. The high exposure on the palm of the hands was most probably as a result of inadequate chemical protection provided by the gloves or due to contamination occurring as a result of incorrect donning and doffing of the gloves. The workers in Area B had the highest exposure levels because it is a enclosed primary dissolve area, where the final concentrate (FICO) was transferred from solid to solution form.

Conclusions: In this study, the wipe removal method, confirmed quantifiable levels of dermal exposure to PGMs in a precious metals refinery. The highest overall exposure occurred in Area B, on the palm of the hands and before lunchtime.

Keywords: platinum, palladium, rhodium, ruthenium, iridium, osmium, skin exposure, sensitisation, wipe sampling.

3.2. Introduction

South Africa is amongst the largest producers in the world of platinum group metals (PGMs) and its by-products (Seymour & O'Farrell, 2001). Production of PGMs worldwide, has risen steadily over the years until recently, with the industry being hampered by labour unrest in South Africa (Wiseman & Fathi, 2009; Chamber of Mines of South Africa, 2014). PGMs are an important source of income for South-Africa. Its high value and uses in a wide variety of industrial, electrical, chemical and pharmaceutical applications makes it very popular amongst various countries (Wiseman & Fathi, 2009; Chamber of Mines of South Africa, 2010). The PGM mining industry was responsible for 23% of South Africa's mining exports (Chamber of Mines of South Africa, 2014). In the process of refining platinum, platinum salts are formed. Both ammonium tetrachloroplatinate and ammonium hexachloroplatinate, present as compounds during the refining process, were found to be the main occupational sensitising agents among platinum refinery workers (Murdoch *et al*., 1986).

PGMs can enter the body through several routes of exposure. It can be ingested, inhaled or come into contact with the eyes or skin. This exposure can result in allergic reactions and result in conjunctivitis, asthma, rhinitis and contact urticaria (Merget *et al.,* 2000). The most documented route of exposure in workplaces is the respiratory route. Some of the most common sources of respiratory exposure to soluble platinum and its compounds are catalyst manufacturing plants and platinum refining (Bolm-Audorff *et al.,* 1992; Ravindra *et al*., 2004). Workers in occupational settings are generally issued with a set of personal protective equipment (PPE) including an overall, safety shoes, a hardhat, safety glasses, hearing protection and a respirator if needed. When wearing this PPE, it covers all the major anatomical areas except for the wrists, the necks and parts of the face and this formed part of the motivation behind the choice of anatomical areas to sample. Tables 1-5 illustrates that exposure occurred on each of these anatomical areas that were not covered in full by the PPE. Exposure can occur when a substance enters, comes into contact or settles on an exposed anatomical area and then transfers through the skin and contributes to the systemic load (Semple, 2004).

An article by Maynard *et al.* (1997) reported that workers who were exposed to platinum compounds via the respiratory route, now suffer from the symptoms consistent with platinum-specific allergenic sensitisation or otherwise known as platinum salt sensitivity (PSS) (WHO, 1991; Maynard *et al*., 1997). Twenty-three percent of a workforce, in a platinum refinery reported symptoms such as dyspnoea, cough, rhinitis and conjunctivitis on a respiratory questionnaire (Bolm-Audorff *et al.,* 1992). Other symptoms such as asthma and chronic bronchitis were reported by the workforce in another platinum refinery (Brooks *et al*., 1990).

Airborne PGMs have the ability to cause adverse health effects in precious metal refinery workers, however all historical respiratory exposure measurements done in the refinery where this study was conducted, indicated results below the OEL (Personal communication – onsite occupational hygienist, C.

Venter). Therefore, the possibility exists that some of the symptoms experienced by workers may be the result of exposure via the respiratory route, the dermal route or a combination of routes (Maynard *et al.,* 1997). Maynard *et al.* (1997) suggested the possibility that the dermal route may be a possible route of exposure to PGMs contributing to sensitisation. The complex salts (tetrachloroplatinate and hexachloroplatinate) of platinum produced during the refining process, are the sensitisers of the platinum compounds (Roberts, 1951; Parrot *et al*., 1969; Cleare *et al*., 1976). The platinum compounds that are eliciting reactions consist of charged compounds containing reactive ligand systems, such as chloride and its allergenicity are related to their charge and overall reactivity. Small doses of platinum salts can cause reactions in sensitised workers (Cleare *et al*., 1976).

During the past forty five years multiple strategies and measurement methods to evaluate dermal exposure have been developed. Some of the methods include interception methods, fluorescent tracer methods and removal methods (Fenske, 1993; Brouwer *et al*., 2000; Soutar *et al.,* 2000; Du Plessis *et al*., 2008). The removal method was used in this study since it is one of the most accepted and commonly used sampling methods for metals that provide useful information about the mass of the contaminant on a surface. The removal method, with Ghostwipes™, as the sampling media in this study, was reported by the Occupational Safety and Health Administration's Method ID125G, to be very successful when removing metals from surfaces (OSHA, 2002). The skin wipe sampling method has been used successfully to quantify exposures to a variety of metals such as nickel, beryllium, cobalt and chromium (Fenske, 1993; HERAG, 2007; Du Plessis *et al*., 2010).

Even though all these measurement methods for dermal exposure exist, there are no dermal occupational exposure limits available to compare the results (Du Plessis *et al*., 2010). It is also unclear whether respiratory exposure or a combination of respiratory and dermal exposure is involved in sensitisation cases, and for this reason it is important to determine the contribution of dermal exposure to the total exposure that could lead to sensitisation.

The aim of this pilot study was to assess dermal exposure to PGMs during the refining process using a removal method and to compare dermal exposure for the PGMs on each of the different anatomical areas and in both the production areas of the refinery.

3.3. Methods

3.3.1. Workplace description

The production process at the Precious Metals Refinery is one of the most challenging and complex of metal separations. The process starts when matte received from the Base Metals Refinery is roasted and sent through a high pressure leaching- and ion exchange process to remove the last traces of copper, nickel, iron and sulphur (Gouldsmith & Wilson, 1963). The PGM solution undergoes precipitation of the metals as powders which is followed by recrystallisation and calcinations under controlled conditions to produce the PGMs in the form of salts. Hydrochloric acid and chlorine gas are the main contributors in the formation of metal salts. The soluble metals (palladium, platinum and gold) are dissolved in ammonium chloride or hydrochloric acid (which then precipitates ammonium hexachloroplatinate) and chlorine gas and they are obtained first in the refining process. The insoluble PGMs (iridium, osmium, rhodium and ruthenium) are obtained last in the process (Seymour & O'Farrell, 2001). The salts formed in the process will be encountered mostly as a result of the refining processes in Level 2 of the refinery, where this study was conducted (Personal communication – onsite occupational hygienist, C. Venter).

Both of the working areas, Area A and B, in which the workers participated are situated in Level 2 of the refinery. Area A is an open area (natural ventilation can take place - area is partly open to the outside air) where one of the last stages of the process takes place. This is where PGMs are recovered from left over process solution (solution that is left, after it went through various processes to remove the other PGMs from the solution). Area B is a enclosed area (no natural ventilation can take place – the area is inside an enclosed building) where one of the first stages in the process of refining PGMs takes place. This is the area where the final concentrate (FICO) is received. Workers may be exposed to PGMs when routine tasks such as digging glove boxex are being done (Personal communication – onsite occupational hygienist, C. Venter). These two areas were both identified as high risk areas by the occupational hygienist on site, because workers complained of skin irritation. Historic respiratory exposure to the PGMs in these two areas was well below the occupational exposure limit. Workers in the Administration area (Level 1) were used as a control group in this study.

3.3.2. Selection of work areas and workers

Before selecting workers to take part in the study, informed consent, from management, the labour unions on site and the workers were obtained. The workforce in these two areas consisted of 6-7 workers per shift per production area. Briefing sessions were held with all the workers in the two production areas to give the workers information on exactly why, how and when the samples were going to be taken and what would be expected of them throughout the study. The sampling took place over three consecutive days in which fifteen workers from the production areas and three from the administration area were selected randomly, to take part in this study. All the names of the workers eligible for participation were listed and every third worker on that list was approached and asked to take part in this study. If the worker declined, the next worker on the list was asked to take part. This was a pilot study and a limited number of samples were collected, therefore, only the day shift workers were included.

Fifteen of the eighteen workers, included in this study, were from the two high risk areas (seven from Area A and eight from Area B).

3.3.3. Sampling strategy

The sampling method was designed to quantify the extent of dermal exposure (mass of PGMs) on the surface of the skin.

3.3.4. Sampling and analysis of samples

A removal method was used to collect samples from the skin by wiping the skin surface with a commercially available skin wipe. The Ghostwipe^{TM}, is individually wrapped and moistened with distilled water by the manufacturer. Every wipe is a separately packaged non-woven fabric sheet.

The anatomical areas included were skin areas that were continuously exposed to the environment (e.g. neck) as well as areas that were partially covered by overalls or gloves (e.g. palm of hand, wrist). Wipe samples were collected prior to the shift, prior to tea and prior to lunch and at the end of the work shift, before the workers washed their hands to ensure samples that represent the worker' actual exposure throughout the work shift.

The same researcher wearing a clean pair of disposable vinyl gloves for each sample conducted all the sampling. Templates made of acetate paper with a rectangular aperture of 24 cm^2 were placed on the sampling area and was held in place by the researcher with one hand while using the other hand to wipe the skin. A clean template was used for each sample taken. The surface was wiped with firm pressure, across the contaminated area with one wipe in an s-motion, covering the entire surface in the template from end to end. The exposed wipe was folded inward. Using the once folded wipe, the area was wiped again starting from the right angles to the first wipe. The wipe was folded inward. Using the twice folded wipe, the same area was wiped from the original starting point. The wipe was folded inward again and wiped for the last time in the same way as the second wipe, before being placed in the vial. In total, each area was wiped four times using one Ghostwipe^{TM}. A total of 12 samples per worker per day (1 wipe x 3 anatomical areas x 4 intervals a day) were collected. One field blank per worker was collected per day. This field blank was handled in the same way as the other wipes; it was taken out of the packaging and placed in the vial in the same environment as the samples taken on the workers.

Wipes were transported to the laboratory in 50 ml plastic vials. Wipes were sent to an accredited laboratory for analysis according to the Methods for the Determination of Hazardous Substances (MDHS) method 46/2, using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The minimum level of detection for this method was 0.083 ng/cm^2 for soluble iridium, platinum, rhodium and ruthenium compounds, 0.417 ng/cm^2 for palladium and 2.5 ng/cm^2 for osmium compounds and skin loading was expressed as nano grams metal per square centimetre (ng/cm^2).

3.3.5. Statistical analysis

The majority of the dermal exposure results were below the analytical limit of detection (BDL). These values were grouped and substituted by making use of a β-substitution method (Ganser & Hewett, 2010). The different categories of exposure data that had less than three values above the limit of detection, was substituted by dividing the limit of detection value by the square root of 2 (Ganser & Hewett, 2010). β-substitution was done for palladium (palm of the hand, wrist and neck before shift), ruthenium (palm of the hand before lunch) and iridium (palm of the hand before tea and neck before shift).

All results were statistically analysed using Statistica Version 11.0 (Statsoft Inc., 2011). Data were skewed and were, therefore, log-transformed. Descriptive statistics (geometric mean, standard error of the mean, etc.) were obtained for the exposure data. Statistical tests such as Bonferroni and Unequal N HSD post–hoc test were firstly done by using all the data from the different anatomical areas and also the different time intervals together, excluding the administration area results, to gain information on where the highest exposure occurred. This data are not displayed in the results and was done to obtain interactions in the results as a starting point. Secondly, Bonferroni tests and independent t-tests (by groups) were done on specific groups of results, observing the production areas and metals over the different time intervals individually, as shown in the results. Bonferroni and independent t-tests were done to determine whether there is a statistically significant difference between the means of two unrelated groups or variables in an analysis of variance. All the results with a $p \leq 0.05$ were considered to be statistically significant. The data described by the geometric mean (i.e. the antilog of the mean of the logarithms of the data) indicate the central tendency or typical value of a set of data. The Administration area's results were constantly the same (BDL) throughout the study and, therefore, could not be included in the statistical analysis.

3.4. Results

Workers who participated in this study (n = 18) worked in the refinery environment for an average of 9.4 years (minimum: 1 year; maximum: 23 years). Thirty seven point five percent of workers in Areas A and B reported that they have experienced irritated skin while working in the refinery. All of the workers were issued with two piece 100% cotton overalls, safety boots, cotton and rubber gloves (Sani-fresh lining), hardhats, safety glasses, earplugs and full-face respirators (with ABEK cartridges and P3 filters) or airstream helmets depending on the area in which they worked.

Of all the dermal wipes, 36.1% analysed for iridium, 54.6% for palladium, 24.1% for platinum, 31.6% for rhodium, 36.1% for ruthenium and 99.5% for osmium were BDL and represented samples collected from all anatomical areas and intervals throughout the day. Osmium was excluded from the statistical analysis due to the majority of results being below the limit of detection. The one value that was above the detection limit for osmium was 4.8 ng/cm^2.

The statistical tests (repeated measures analysis of variance with effect sizes and powers, Bonferroni and Unequal N HSD post–hoc test) that was done on the results as a whole, showed significant interactions between anatomical areas, work areas and the intervals sampled during the shift for platinum ($p = 0.007$), indicating that these factors were associated with one another when changes occurred, e.g. when platinum exposure on the palm of the hand increased, it also increased on the wrist and the neck before the shift commenced. For palladium, ruthenium and iridium there were no statistical significant interactions between any of the three factors. For rhodium there were significant interactions between the work areas and anatomical areas ($p = 0.02$) and the work areas and the intervals throughout the shift ($p = 0.0007$).

Dermal exposure to the individual PGMs are summarised in Tables 1 to 5. It indicates the exposure measured in the two production areas (Area A and B) on each of the anatomical areas (palm of hand, wrist and neck) of the different intervals during the 8 hour work shift. Results of all field blanks and the majority of the administration area (control group) samples analysed, were BDL. There were three palladium samples in the administration area, taken on the neck before tea time which was equal to the detection limit (0.42 ng/cm^2).

Results in Tables 1 to 5 indicate that production workers had detectable levels of iridium, palladium, platinum, rhodium and ruthenium on their skin throughout the work shift. On the majority of the samples, some level of these PGMs could be detected even before the shift started. Platinum exposure was the most prominent, followed by palladium and iridium. Evident from some of the metals' geometric means (GM) was that in most instances the overall highest exposure occurred before lunch time and at the end of the shift. The anatomical area that had the highest exposure was the palm of the hand with levels ranging between 0.14 ng/cm^2 and 3.02 ng/cm^2.

Table 1: Platinum dermal exposure (ng/cm^2) of 15 production workers measured with the wipe sampling method.

		GM	Standard Error (GM)	Minimum	Maximum
Palm of hand	Before shift	0.59 [a, b, c, d, e]	0.13	0.17	3.00
	Before tea	2.02 [a, f, g,]	0.63	0.19	9.09
	Before lunch	3.02 [b, h]	0.69	0.47	9.09
	End of shift	2.25 [c, i, j]	0.60	0.24	12.43
Wrist	Before shift	0.16 [d, k, l, m]	0.07	BDL	2.50
	Before tea	0.79 [f, k]	0.32	BDL	10.76
	Before lunch	1.39 [l]	0.60	BDL	12.58
	End of shift	0.99 [i, m]	0.29	0.11	8.26
Neck	Before shift	0.10 [e, n, o, p]	0.03	BDL	0.92
	Before tea	0.63 [g, n]	0.24	BDL	13.42
	Before lunch	0.92 [h, o]	0.23	0.08	2.93
	End of shift	0.74 [j, p]	0.13	0.15	1.93

BDL – Below detection limit

a-p represents significant differences between anatomical areas and intervals during the shift.

Table 1 shows that dermal exposure was present on the skin of the workers before the shift commenced. There were significant differences between exposure on all of the anatomical areas (palm of hand, wrist and neck) before the shift started with all of the other time intervals (before tea, before lunch and end of the shift). Throughout the shift there was significantly higher exposure on the palm of the hand than on the wrist and neck. The highest exposure occurred before lunch on all the anatomical areas, with exposure on the palm of the hand being the highest.

Table 2: Palladium dermal exposure (ng/cm^2) of 15 production workers measured with the wipe sampling method.

		GM	Standard Error (GM)	Minimum	Maximum
Palm of hand	Before shift	BDL	0.03	BDL	1.25
	Before tea	0.45 [a]	0.14	BDL	4.04
	Before lunch	BDL	0.10	BDL	4.21
	End of shift	BDL	0.07	BDL	6.79
Wrist	Before shift	BDL	0.02	BDL	0.83
	Before tea	BDL [a*]	0.04	BDL	3.54
	Before lunch	0.43	0.24	BDL	38.96
	End of shift	BDL	0.04	BDL	11.46
Neck	Before shift	BDL	0.06	BDL	2.08
	Before tea	BDL	0.05	BDL	8.96
	Before lunch	BDL	0.08	BDL	5.71
	End of shift	BDL	0.03	BDL	1.96

BDL – Below detection limit

a represents the significant difference between anatomical areas before tea.

* Represents results on which β-substitution was done for statistical analysis which indicated a significant difference; and to simplify the results BDL was used instead of the β-substitution value.

There were significant differences between the before shift and end of shift exposure to palladium exposure ($p = 0.0002$) and also between the before lunch and end of shift exposure ($p = 0.0033$) (based on overall palladium exposure – not indicated in Table 2). The only exposure that was not below the detection limit was on the palm of the hand before tea and on the wrist before lunch. The anatomical area and time interval that had the highest exposure was the palm of the hand before tea time.

Table 3: Rhodium dermal exposure (ng/cm^2) of 15 production workers measured with the wipe sampling method.

		GM	Standard Error (GM)	Minimum	Maximum
Palm of hand	Before shift	0.24 [a, b, c]	0.04	0.17	1.00
	Before tea	0.59 [d]	0.13	0.09	1.98
	Before lunch	0.80 [a, e, f]	0.16	0.32	3.23
	End of shift	0.68 [g]	0.15	BDL	3.57
Wrist	Before shift	0.10 [b, h, i, j]	0.03	BDL	0.71
	Before tea	0.34 [h, k]	0.12	BDL	3.82
	Before lunch	0.42 [e, i, l]	0.11	0.11	2.65
	End of shift	0.27 [j]	0.09	BDL	2.32
Neck	Before shift	0.09 [c, m]	0.02	BDL	0.46
	Before tea	0.13 [d, k]	0.04	BDL	0.98
	Before lunch	0.22 [f, l, m]	0.04	0.08	0.79
	End of shift	0.15 [g]	0.03	BDL	0.56

BDL – Below detection limit

a-m represents significant differences between anatomical areas and intervals throughout the shift.

The exposure before the shift commenced was the lowest on all the anatomical areas. There were significant differences between exposure on the wrist before the shift commenced, and all the other intervals. The palm of the hand had the highest rhodium exposure, followed by the wrist and the neck. There were statistical significant differences between all of the anatomical areas between the before shift and before lunch exposures.

Table 4: Ruthenium dermal exposure (ng/cm^2) of 15 production workers measured with the wipe sampling method.

		GM	Standard Error (GM)	Minimum	Maximum
Palm of hand	Before shift	0.18 [a, b, c]	0.03	BDL	0.92
	Before tea	0.72 [a]	0.18	0.10	3.00
	Before lunch	0.80 [b]	0.20	0.08	4.58
	End of shift	0.96 [c]	0.20	0.24	5.75
Wrist	Before shift	BDL [d, e, f *]	0.02	BDL	1.00
	Before tea	0.28 [d]	0.09	BDL	5.25
	Before lunch	0.46 [e]	0.13	0.08	3.92
	End of shift	0.38 [f]	0.10	BDL	2.92
Neck	Before shift	BDL [g, h, I *]	0.01	BDL	0.42
	Before tea	0.15 [g, j]	0.04	BDL	0.63
	Before lunch	0.26 [h, j]	0.04	0.09	1.17
	End of shift	0.21 [i]	0.03	BDL	0.53

BDL – Below detection limit

a-j represents significant differences between anatomical areas and intervals throughout the shift.

* Represents results on which β-substitution was done for statistical analysis which indicated a significant difference; and to simplify the results BDL was used instead of the β-substitution value.

The before shift exposures were the lowest of all the time intervals. The palm of the hand had the highest ruthenium exposure for all the time intervals. There were significant differences between the palm of the hand and the neck before the shift started and all of the other time intervals. Exposure increased from the beginning of the shift towards lunch time and the end of the shift. The highest exposure occurred on the palm of the hand at the end of the shift (0.96 ng/cm^2).

Table 5: Iridium dermal exposure (ng/cm^2) of 15 production workers measured with the wipe sampling method.

		GM	Standard Error (GM)	Minimum	Maximum
Palm of hand	Before shift	0.20 [a, b, c, d]	0.05	BDL	1.08
	Before tea	0.87 [a]	0.19	0.13	2.92
	Before lunch	1.19 [b, e, f]	0.24	0.42	4.00
	End of shift	1.20 [c, g, h]	0.31	0.13	6.08
Wrist	Before shift	0.18 [i, j, k]	0.03	0.08	0.92
	Before tea	0.26	0.09	BDL	3.33
	Before lunch	0.49 [e. i]	0.15	0.08	3.42
	End of shift	0.41 [g, j]	0.13	0.08	2.58
Neck	Before shift	BDL [d, k *]	0.01	BDL	0.75
	Before tea	BDL	0.0	BDL	BDL
	Before lunch	0.25 [f]	0.06	BDL	0.83
	End of shift	0.22 [g, h]	0.05	BDL	1.92

BDL – Below detection limit

a-k represents significant differences between anatomical areas and intervals throughout the shift.

* Represents results on which β-substitution was done for statistical analysis which indicated a significant difference; and to simplify the results BDL was used instead of the β-substitution value.

Exposure before the shift commenced was the lowest of all the time intervals sampled. Exposure on the palm of the hand was significantly higher than that of the wrist and neck for all the time intervals. Exposure on the palm of the hand was four times higher than that of the wrist.

Comparison of exposure between the two production areas:

Tables 6 to 10 are a representation of the exposure detected on each of the anatomical areas (palm of hand, wrist and neck) throughout the different intervals (before shift, before tea, before lunch and end of shift) in the 8 hour work shift in each of the two production areas in the refinery.

Observing the geometric means (GM) of all the PGMs in the two production areas, the highest exposure, in most instances, occurred before lunch and at the end of the shift. The anatomical area that had the highest exposure to most of the PGMs was the palm of the hand. Based on the geometric means, the workers in Area B had higher exposure to palladium, platinum, rhodium and ruthenium and the workers in Area A had the highest exposure to iridium.

Table 6: Platinum dermal exposure (ng/cm^2) of 15 production workers measured with the wipe sampling method in two production areas.

		Area A		Area B	
		GM	Standard Error (GM)	GM	Standard Error (GM)
Palm of hand	Before shift	0.337 [a]	0.064	0.964 [a]	0.262
	Before tea	0.995 [b]	0.546	3.756 [b]	0.523
	Before lunch	2.838	1.073	3.184	0.932
	End of shift	1.500	0.433	3.195	0.128
Wrist	Before shift	BDL	0.057	0.312	0.120
	Before tea	0.442	0.346	1.324	0.353
	Before lunch	1.088	0.955	1.717	0.550
	End of shift	0.683	0.358	1.364	0.374
Neck	Before shift	BDL	0.033	0.145	0.062
	Before tea	0.283 [c]	0.151	1.265 [c]	0.533
	Before lunch	0.750	0.374	1.105	0.179
	End of shift	0.754	0.214	0.721	0.175

BDL – Below detection limit

a-c represents significant differences between exposure in the two production areas.

In both the production areas, there were detectable levels of platinum on all the anatomical areas before the shift commenced except in Area A on the wrist and the neck. The highest exposure occurred in Area B and at the intervals before tea towards the end of the shift. There were significant differences between Area A and B on the palm of hand before shift and before tea results as well as on the neck before tea results.

Table 7: Palladium dermal exposure (ng/cm^2) of 15 production workers measured with the wipe sampling method in two production areas.

		Area A		Area B	
		GM	Standard Error (GM)	GM	Standard Error (GM)
Palm of hand	Before shift	BDL	0.015	BDL	0.064
	Before tea	0.626	0.328	BDL	0.116
	Before lunch	BDL	0.082	0.447	0.237
	End of shift	BDL	0.063	BDL	0.142
Wrist	Before shift	BDL [a *]	0.015	BDL [a *]	0.044
	Before tea	BDL	0.091	BDL	0.039
	Before lunch	BDL	0.176	0.843	0.589
	End of shift	BDL	0.036	BDL	0.087
Neck	Before shift	0.499 [b]	0.170	BDL [b *]	0.0001
	Before tea	BDL	0.0003	BDL	0.151
	Before lunch	BDL	0.031	BDL	0.285
	End of shift	BDL	0.079	BDL	0.030

BDL-Values below the detection limit

a-b represents significant differences between exposure in the two production areas.

* Represents results on which β-substitution was done for statistical analysis which indicated a significant difference; and to simplify the results BDL was used instead of the β-substitution value.

There were two statistical significant differences between Area A and B for palladium; at the wrist and neck before shift. The highest exposure in Area A occurred on the palm of the hand before tea time and in Area B on the wrist before lunch.

Table 8: Rhodium dermal exposure (ng/cm^2) of 15 production workers measured with the wipe sampling method in two production areas.

		Area A		Area B	
		GM	Standard Error (GM)	GM	Standard Error (GM)
Palm of hand	Before shift	0.225	0.038	0.371	0.071
	Before tea	0.418	0.150	0.813	0.187
	Before lunch	0.613	0.182	1.001	0.267
	End of shift	0.421 [a]	0.140	1.045 [a]	0.233
Wrist	Before shift	BDL	0.031	0.139	0.053
	Before tea	0.297	0.226	0.375	0.074
	Before lunch	0.413	0.150	0.426	0.162
	End of shift	0.164	0.091	0.405	0.127
Neck	Before shift	BDL	0.017	0.117	0.035
	Before tea	BDL	0.035	0.210	0.074
	Before lunch	0.158	0.032	0.294	0.077
	End of shift	0.115	0.028	0.188	0.044

BDL – Below detection limit

a represents the significant difference between exposure in the two production areas.

Exposure before the shift commenced for each of the anatomical areas in Area A and B was generally the lowest. There was a significant difference between the palm of the hand end of shift results between Area A and B. The highest exposure in Area A and B occurred on the palm of the hand before lunch and at the end of the shift.

Table 9: Ruthenium dermal exposure (ng/cm^2) of 15 production workers measured with the wipe sampling method in two production areas.

		Area A		Area B	
		GM	Standard Error (GM)	GM	Standard Error (GM)
Palm of hand	Before shift	0.139	0.029	0.215	0.048
	Before tea	0.556	0.249	0.894	0.249
	Before lunch	0.622	0.258	1.008	0.312
	End of shift	0.653	0.115	1.332	0.428
Wrist	Before shift	0.088	0.043	BDL	0.012
	Before tea	0.299	0.183	0.265	0.095
	Before lunch	0.439	0.203	0.485	0.188
	End of shift	0.285	0.143	0.493	0.120
Neck	Before shift	BDL	0.021	BDL	0.006
	Before tea	0.097	0.041	0.208	0.073
	Before lunch	0.202	0.043	0.335	0.072
	End of shift	0.193	0.052	0.224	0.034

BDL – Below detection limit

Exposure in both the areas increased towards lunch. Exposure before the shift commenced was the lowest in both the areas. The highest exposure in Area A and B occurred on the palm of the hand at the end of the shift. There were no significant differences between exposure in Area A and B.

Table 10: Iridium dermal exposure (ng/cm^2) of 15 production workers measured with the wipe sampling method in two production areas.

		Area A		Area B	
		GM	Standard Error (GM)	GM	Standard Error (GM)
Palm of hand	Before shift	0.199	0.064	0.197	0.069
	Before tea	0.945	0.404	0.811	0.165
	Before lunch	1.440	0.838	1.011	0.319
	End of shift	1.141	0.417	1.254	0.487
Wrist	Before shift	0.220	0.053	0.153	0.024
	Before tea	0.309	0.189	0.230	0.085
	Before lunch	0.549	0.238	0.448	0.196
	End of shift	0.361	0.174	0.465	0.186
Neck	Before shift	0.085	0.031	BDL	0.0001
	Before tea	BDL	0.0001	BDL	0.0002
	Before lunch	0.269	0.112	0.237	0.050
	End of shift	0.250	0.116	0.203	0.034

BDL – Below detection limit

Exposure in Area A and B was the highest on the palm of the hands. In most instances exposure was the lowest before the shift commenced. The highest exposure in Area A and B occurred on the palm of the hand before lunch and at the end of the shift. There were no significant differences in iridium exposure between Area A and B.

3.5. Discussion

Dermal exposure to PGMs in the precious metals refinery was confirmed with a removal method using Ghostwipes™. This removal method is designed to measure the total concentration (dose) of metals that was deposited onto the skin surface. The majority of the results were below the analytical detection limit which does not mean that there was no exposure; it only states that the exposure could not be detected with the atomic absorption spectrometer used for the analysis. The osmium results had only one measurement (4.8 ng/cm^2) that was not below the detection limit of 2.5 ng/cm^2. Some of the other PGMs such as platinum had exposure levels of 0.08 ng/cm^2 which is lower than the above mentioned detection limit even though it would not be quantified by the current analysis method. This analytical method will cause problems in future studies with the results that were limited due to the detection limit being too high. This level of exposure could still cause adverse health effects because sensitisation can occur at levels rarely exceeding the OEL (Manyard *et al.,* 1997). The removal method confirmed the first objective that dermal exposure to all six the PGMs took place with platinum exposure being the highest, based on the geometric means (Table 1).

Hughson *et al*. (2010) reported background levels of nickel on the hands and forearms of workers whilst Du Plessis *et al.* (2010) reported exposure to nickel on the skin of workers in a base metals refinery, before the shift commenced. This study confirmed the presence of PGMs before the shift commenced (Tables 1-5). This pre-shift exposure could be the result of contamination that took place in the change houses (benches, lockers, PPE, etc.), loading of metals on the skin from the previous shift or poor personal hygiene. Du Plessis *et al*. (2010) reported that surfaces (lockers, overall collection counter, etc.) in the change house at the refinery were contaminated with nickel levels varying between 3.879 and 794.739 ug. At the refinery used in this study, when the workers arrived at work, they had to proceed through change houses and dress in clean overalls before entering their work stations. Contamination of the palm of the hand and the wrist could have taken place when the workers touched their lockers or clean overalls. The overalls might have been contaminated during the wash and drying process when e.g. the clean overalls were placed on dirty benches when they were folded, and this could contribute significantly to contamination prior to the shift. The hardhats were removed and stored in the lockers at the end of the shift and in this way contamination could also have occurred because the hardhats were not washed or decontaminated between shifts. The handles of the lockers, toilets, bathroom and change house doors could also have been contaminated throughout the day, and in this way, cause further contamination with every new shift when workers enter the change house and open their lockers.

The PGM exposure before tea time for platinum, ruthenium and iridium were lower than the before lunch time and end of shift exposures based on the geometric means (Tables 1-5). This could be explained by the majority of the workers doing housekeeping or cleaning from the beginning of the shift until tea time, whilst some of them were in meetings.

The highest exposure took place predominantly in the periods after tea time where in some instances the exposure was the highest before lunch and in other instances the exposure was the highest at the end of the shift for platinum, rhodium, ruthenium and iridium (Tables 1-5). During these time periods the workers in both the production areas dropped hoppers, dug glove boxes, checked equipment, cleaned filters and flushed and loaded tanks which are all tasks where the risk of exposure exist. Samples were collected from the ventral surfaces of the hand and wrist. When the workers dig the glove boxes the PGMs are in a powder form and, depending on the worker digging the glove box, the PGM's sometimes manage to escape when they open the glove boxes and dig them. There was still some exposure on the palm of the hands while wearing cotton and rubber gloves and this is possibly an indication that the protection provided by the gloves was inadequate. Alternatively, some of the PGMs could have managed to get in through the opening at the top of the glove or when workers removed their gloves before removing their hardhats, safety glasses and earplugs and in this way touching the dirty PPE with their bare hands causing contamination. They could possibly have removed their gloves on a regular basis throughout the shift, causing contamination with wrongful donning and doffing of gloves. Before tea and lunch time the workers put their hard hats on hooks on the tearoom wall and went into the change houses where they removed their gloves before washing their hands; contamination could have occurred when some of the workers used their dirty overalls that they were still wearing to dry their hands or they touched the contaminated part of the gloves after removal and placement in the lockers. Of the three anatomical areas included in this study, the palm of the hand, which was protected by a cotton and rubber glove, had the highest exposure to all of the PGMs followed by the wrist and the neck (Tables 1-5). In the authors' opinion the majority of the exposure occurred as a result of contamination moving in and out of the change houses and canteens and not in the production areas.

Based on the geometric means of the two production areas, the metal to which the workers in Area A and B had the highest exposure was platinum (Tables 6-10). When observing both the production areas, the worker's exposure to palladium, platinum, rhodium and ruthenium was the highest in Area B (based on GM). Iridium exposure was slightly higher in Area A than in Area B (based on GM). The production process in Area B is of such a nature that the FICO that is received and processed, are in solution form most of the time, and the solution travels along pipes and tanks from one part of the process to the next. At some stages throughout the process the PGMs are in a powdery form, for instance in the glove boxes. The exposure that occurred in this study in Area B could have occurred when workers dug glove boxes and some of the PGMs escaped into the air (of which some could not have been removed by extraction ventilation) and came into contact with the sampled anatomical areas (palm of hand, wrist and neck) or the workers came into contact with the PGMs with their gloves. As Area B is a confined area, the PGMs that escaped into the air could have accumulated in the air or on surfaces and thus, in this way, caused exposure. In contrast with Area B, the production process in Area A, where the PGMs are recovered out of left over process solution, has powder forms of PGMs in the process in most instances.

Area A has extraction ventilation systems on certain machinery but no area ventilation. If the powder forms of the PGMs are handled, it may disperse into the air and accumulate on surfaces or be influenced by the natural ventilation taking place and in this way contamination can occur when workers touch contaminated surfaces.

The workers in the administration area were included as a control group in this study as it is not a production area and was not expected to have any PGM exposure. In this area, administration work is done and the workers did not access the plant. Most of the results of the administration area samples were below the detection limit, except for three samples for palladium which equalled the detection limit (0.42 ng/cm^2 on the neck before tea time). The only possible place where exposure or cross-contamination could have occurred was in the canteen, where some production workers had lunch with the administration area workers. To ensure that cross-contamination does not take place the level 1 and 2 workers should have lunch in their respective canteens to prevent contamination occurring.

Du Plessis *et al*. (2010) stated that direct and prolonged contact with nickel metal can lead to skin sensitisation in workers that would normally result in allergic contact dermatitis. No published data exists on PGMs permeation through the skin, thus the possibility thereof cannot be excluded from this study. Manyard *et al.* (1997) suggested that the dermal route may be a possible route of exposure contributing to sensitisation. Dermal exposure is a very serious health risk that should be measured more frequently. Du Plessis *et al.* (2010) proved that refinery workers' skin is sometimes compromised and damaged throughout the process. Larese Filon *et al.* (2009) proved that permeation increases through damaged skin. Thus, refinery workers have a higher risk of exposure occurring and serious health risks arising. This study proved that dermal exposure to platinum, palladium, rhodium, ruthenium and iridium in a refinery setting occurred. Dermal exposure at a precious metals refinery could possibly contribute to sensitisation and the symptoms associated with it occurring. This highlights the importance to eliminate even the slightest risk of exposure occurring.

3.6. Conclusion

This pilot study established that quantifiable levels of dermal exposure to PGMs in a precious metals refinery did occur, thus the hypothesis is accepted. Although the majority of the results were below the detection limit, all the anatomical areas were exposed to detectable levels of PGMs. The exposure before the shift commenced is upsetting as there should not be any exposure whatsoever. The production area, anatomical area and time interval during the day that had the highest exposure were Area B, the palm of the hand and before lunch time. When dermal exposure takes place, the possibility of permeation exists and this could lead to sensitisation. More PGM studies are needed at refineries, with larger sampling groups, to obtain more information concerning dermal exposure and sensitisation in refineries and to implement controls specifically to prevent dermal exposure.

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CHAPTER 4: CONCLUDING CHAPTER

In this final chapter, conclusions will be made with regards to the aims, objectives and the hypothesis of the study. Recommendations will be made to the precious metals refinery in an attempt to reduce dermal exposure to PGMs. Limitations of this study and possible future studies will be discussed.

4.1. Conclusions

Numerous researchers used surrogate skin methods (interception methods), removal methods or florescent tracer methods (*in situ* detection methods) to determine the dermal exposure to occupational and environmental substances (Fenske, 1993; Brouwer *et al*., 2000; Cherrie *et al*., 2000; Soutar *et al*., 2000; Du Plessis *et al.,* 2010). It is evident according to previously published literature that the wipe sampling method (dermal removal method) is the most popular and successfully used sampling method to remove metals from surfaces and to obtain the concentrations thereof (Davis *et al*., 1983; Fenske, 1993; Schneider *et al*., 2000; OSHA, 2002; Lidén *et al*., 2006; Day *et al*., 2007; HERAG, 2007; Du Plessis *et al*., 2010; Christopher *et al*., 2011). The samples in this study were analysed by an accredited laboratory according to the Methods for the Determination of Hazardous Substances 46/2. The majority of the results were below the analytical detection limit, especially the osmium results. This does not mean that there was no exposure; it only states that the exposure could not be detected with the equipment used for the analysis. The laboratory detection limit for soluble iridium, platinum, rhodium and ruthenium was 0.083 ng/cm^2, for palladium it was 0.417 ng/cm^2 and for osmium it was 2.5 ng/cm^2. The osmium detection limit is much higher than the other two detection limits. This could have contributed to almost all the osmium results being below the detection limit and this does not give a true reflexion of the osmium exposure. Although the majority of the results were BDL and it could not be quantified, the possibility of exposure still exists.

Precious metals refinery workers are potentially exposed to PGMs and their metal salt compounds through the dermal route of exposure. Ammonium tetrachloroplatinate and ammonium hexachloroplatinate are intermediates in the refining process and were found to be two of the main occupational sensitising agents (Murdoch *et al*., 1986). A sensitisation reaction occurs when exposure to a substance takes place, which elicits a response in the immune system when an allergen or chemical is absorbed through the skin or the respiratory tract and activates an immune response which can be recalled with a subsequent encounter with the allergen or chemical (McCullough & Summerfield, 2005). Small doses of platinum salts are needed to bring forth reactions in workers that are sensitised. Exposure to these compounds can cause conjunctivitis, contact urticaria, asthma and rhinitis (Merget *et* *al*., 2000). This can affect not only the worker, but also the company regarding lost time in production and compensation to the worker.

The two production areas included in this study were Area A and Area B. Area A is an area where one of the last stages of the process takes place. This is an area where the recovering of PGMs takes place out of left over process solution. This is an open area (natural ventilation can take place - area is partly open to the outside air) where the overall exposure for all the anatomical areas during all the intervals throughout the day, was found to be lower than in Area B. Area B is the materials handling area, where one of the first stages in the process of refining PGMs takes place. This is the area where the FICO (final concentrate) is received and processing of the PGMs takes place. It is also a confined area (no natural ventilation can take place – the area is inside an enclosed building), where the exposure was found to be higher for platinum, rhodium, ruthenium and iridium. The workers in Area B could have come into contact with some forms of the PGMs when they were digging glove boxes or when there were breakdowns. When digging glove boxes, the PGMs could escape into the air and come into contact with some of the sampled anatomical areas. The workers could also have been exposed when the PGMs managed to get into the opening of their gloves, if it went through the gloves or if they made contact with PGMs that settled on the surface of the gloves when they removed the gloves (wrongful donning and doffing of gloves). In a study done on cemented tungsten carbide workers, the results also revealed that exposure on the hands are possibly due to contamination when gloves were removed (Day *et al.,* 2009).

The covered (palm of the hands) anatomical area had more exposure than the uncovered (wrist and neck) anatomical areas. This may be due to contamination occurring when donning and doffing of PPE took place, also due to contamination taking place in the change houses where dirty lockers, locks on the lockers, benches, toilet, basin and door handles were touched with clean hands. The change houses are open to the workers throughout the day, and it is also where they wash their hands before tea time and lunch time. Thus, it is possible for exposure or contamination to occur in the change houses throughout the shift. Another possible source of exposure to the palm of the hands could have been the handling of contaminated gloves when removed.

All the workers and contractors working in the refinery are issued with PPE before entering. The workers have the same PPE for all of the working areas in the refinery, with additional add-ons, like airstream helmets, in areas such as Area A where the risk of dermal exposure is higher than in some other areas in the plant. All of the production workers are issued with two piece 100% cotton overalls, safety boots, cotton and rubber gloves, hardhats, safety glasses and earplugs. The workers in Area B are issued with ABEK-respirators with P3 filters to protect them against unwanted gasses and vapours inside the area and the workers in Area A wear airstream helmets to protect them from inhaling air possibly containing some powdery forms of the PGMs.

- Airstream helmets are designed to draw contaminated air into the blower unit of the helmet and to filter the air as it passes through the filter. Clean air is directed into the back of the helmet and over the face providing fresh air to the wearer to breathe.
- ABEK Respirators are half or full face respirators that can be worn by workers. These respirators offer protection against:

A - Organic vapours and gases with boiling points >65°C

B - Inorganic gases excluding carbon monoxide

E - Sulphur dioxide and acidic gases

K - Ammonia and organic ammonia derivatives

Table 1: PPE used by the workers in the precious metals refinery

Name of the PPE items	Pictures of the PPE
Two-piece 100% cotton overalls	
Safety Boots	
Cotton Gloves	
Rubber Gloves	
Hardhats	
Safety Glasses/Goggles	
Earplugs	
ABEK-Respirators with P3 Filters	 
Airstream Helmets	

The exposure to the PGMs over the different time intervals throughout the day, revealed very low concentrations. Most of the workers had some level of exposure to PGMs on their skin before the shift commenced. Day *et al*. 2009 also stated that pre-shift contamination might have occurred in a study he conducted, as his results revealed some exposure before the shift commenced in cemented tungsten carbide workers. This could be the result of loading of metals on the skin from the previous shift (take home exposure) or because of contamination that took place from when the worker entered the refinery to where the worker came out of the change house before entering the production area. There are various manners in which this contamination could have taken place:

- Clean overalls that the workers put on with every new shift that could have been contaminated during the wash and drying process e.g. when it is folded on contaminated benches or tables,
- hardhats that are not decontaminated or cleaned from one shift to the next and just stored in the lockers after each shift and then touched with clean hands, causing contamination,
- contaminated benches, lockers, basins and other surfaces in the change houses,
- PGM loading from one shift to the next (take home exposure).

The exposure before tea time was lower than before lunch time and at the end of the shift due to the fact that most of the workers had meetings in that time period or had only done cleaning or housekeeping such as making sure cleaning equipment are stored and that the areas are clean and free of objects causing obstruction. The period before lunchtime towards the end of the shift revealed the highest exposure for most of the metals on almost all the anatomical areas.

This could be because the workers had been doing mostly physical work such as digging glove boxes during this interval of the shift. They flushed and loaded tanks, dropped hoppers, checked equipment, cleaned filters and did housekeeping. All of these tasks were fairly physical and the likelihood of exposure was higher as the possibility of contact with the PGMs was higher. With the physical work the workers were in closer contact with some of the PGMs, thus higher exposure occurred. With these tasks at hand and the PPE that does not cover the wrist and neck completely, exposure could have occurred at any time of the day. The possibility of exposure could also have occurred if workers started sweating or itching and touched their necks or faces with the contaminated gloves. Between lunchtime and the end of the shift, the exposure decreased in most instances due to the workers doing general tasks like sweeping and checking equipment.

The results of the administration area in Level 1 of the plant that was used as control subjects, was below the detection limit for all of the PGMs except for three samples for palladium measured on the neck before tea time. This could be as a result of contamination that took place in the Level 1 canteen, where some of the workers of Level 2 had tea or lunch with workers from Level 1. The Level 1 administration workers' hands could have been contaminated when they touched contaminated surfaces in the canteen and from there; they could have contaminated their own necks by touching them with their hands.

Lead exposure was noted in the results when the samples were sent for soluble metal analysis. Traces of lead were found in the majority of the samples and also in the administration area's results, which is a clean isolated area on a different level of the refinery than where the production takes place. Of all the samples taken in this study, lead was detected on 87.1% of them. Lead is an IARC class 2B carcinogen (possible human carcinogen) and this is definite reason for concern. Future studies can include lead into their research and an investigation should be done on where lead exposure originates in the process and at which point workers are exposed. A monitoring programme should be implemented and include regular lead sampling in all the areas (including the low risk areas like the administration area).

As stated earlier, previous research has focused on the respiratory route of exposure as the main route of exposure to various metals and limited information is available on dermal exposure to these metals. The hypothesis stated that workers at a precious metal refinery are exposed to quantifiable levels of PGMs via the dermal route of exposure. This hypothesis is thus partially accepted as the results indicated quantifiable levels of dermal exposure for some of the PGMs such as platinum on all of the anatomical areas throughout all the intervals of each shift. Exposure to osmium, however, could not be quantified due to 99. 5 % of the results being BDL and a quarter to a half of the other PGM' results were also BDL.

4.1.1. Limitations

Limitations related to assessment of dermal exposure to PGMs:

- This method of sampling was new to the workers; they were anxious to be picked for the study at first.
- The time in which the samples had to be taken was limited because it was in the workers' tea time and lunch time.
- The precious metals refinery is a high security plant. It was a complex process to get the sampling media in and out of the plant, especially because it was PGM containing samples and sampling media.
- This was a pilot study containing a limited number of workers, which complicated the data when graphic presentations, statistics and calculations regarding the data had to be compiled.
- The analytical method used in this study had very high detection limits for some of the PGMs and because of this the low level of dermal exposure could not be quantified accurately.

4.1.2. Recommendations

Recommendations for future studies:

- An expansion of the study population, that includes more high (production areas) and low (training or induction areas) risk areas in the refinery are recommended. This would obtain information about where else in the refinery there may be underlying risks involving dermal exposure.
- Surface sampling of work benches, basins, lockers, hardhats, the canteen and the change houses will also contribute to the dermal sampling study, when the possible sources of exposure due to surface contact can be identified.
- Samples (patches) inside PPE such as gloves and overalls could contribute in testing the effectiveness of the PPE issued to the workers.
- Randomly selected clean PPE testing, to see if the washing and drying process does not contaminate the overalls.
- Inclusion of respiratory and biological monitoring and skin condition measurements to compare dermal exposure measurements, would result in more representative and valuable results and would also highlight the contribution of each exposure route (Du Plessis *et al*., 2013).
- Lead sampling should be done on all of the workers as lead was noticed on the analytical report, on all of the anatomical areas during all of the time intervals throughout the day, even in the administration area.

4.2. Recommendations for refineries concerning contamination

- Currently, one locker is allocated to each worker in the different change houses. This is where the workers store their safety shoes and glasses, earplugs and hardhats after the shift ends. The dirty overalls are thrown in an already open washing bin and clean overalls and socks are placed in the lockers for the next shift. The same locker, in which the dirty PPE was stored when the workers' shift has ended, is where the workers' normal clothing was stored during the work shift. By storing the above mentioned PPE in the lockers, there is a good chance of contamination occurring when the workers use their dirty PPE, such as hardhats for each new shift. In this way the lockers also contaminate the workers' normal clothing and this would contribute to take home contamination. It is recommended that when the workers' shift ends, there should be a bin for each item of the PPE, in which the workers can throw their dirty PPE, and then this PPE should be washed and decontaminated before the new shift starts and that separate lockers for clean and dirty PPE are issued to all the workers to eliminate contamination.

- It is recommended that the washing bins are placed in range of the showers to ensure the workers throw their dirty overalls in the bins before taking a shower to prevent contamination occurring after taking a shower, when dirty overalls are handled again.
- Some of the workers wear two pairs of gloves when working, a cotton glove and a rubber glove. All the workers should be encouraged to wear both pairs for better protection. It would also offer some level of protection when work needs to be done on smaller objects, and only one pair of gloves is removed. Nitrile gloves can also be used when work is done on smaller objects.
- The refinery should initiate a skin protection program including training and illustration sessions on the correct donning and doffing procedure of the gloves, to ensure contamination does not occur when doffing the gloves incorrectly or when handling contaminated gloves after doffing.
- When gloves are removed for some reason, they should either be thrown away to avoid contamination or it should be placed somewhere where they can be cleaned and not cause cross contamination to other workers or to surfaces that other workers touch.
- All sensitisers and potential sensitisers on site should be acknowledged and workers should be made aware of the health effects associated with being sensitised.
- Training should be given to workers on basic hygiene and washing and drying of hands to ensure that the hands are not dried on the overalls and that gloves and other contaminated PPE are not touched with bare hands.
- Dermal sampling e.g. skin wipes, can be included in the sampling strategy for the refinery each year, for the PGMs and lead, together with the airborne pollutant sampling results.
- Workers in die production areas and in the administration areas should be prevented from having lunch if they have not washed their hands first, this would prevent hand to mouth contamination.
- Adequate hand wash and dry facilities should be made available to workers before entering canteens.
- Lead sampling can be done on all of the workers as lead was noticed on the analytical report, on all of the anatomical areas during all of the time intervals throughout the day, even in the administration area.
- Regular cleaning in both the areas can be done in the time interval before lunch time and at the end of the shift as this is when the highest exposure occurred in this study.
- Pre-shift contamination and take-home contamination should be minimised and eliminated as far as reasonably possible by good housekeeping and personal hygiene and regular cleaning of change houses, lockers and dirty PPE.

This study assessed dermal exposure of precious metal refinery workers to PGMs. The three specific objectives were met as follows:

- By using a removal method, this study determined that dermal exposure to PGMs occurred during the refining process.
- Dermal exposure on the different anatomical areas was statistically compared for platinum, palladium, rhodium, ruthenium and iridium, but not for osmium.
- Dermal exposure in the two production areas (Area A and B) were statistically compared for platinum, palladium, rhodium, ruthenium and iridium, but not for osmium. Statistical comparisons could not be made for the administration area.

4.3. References

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CHAPTER 5: APPENDIX

5.1. Appendix A: Language editing certificate